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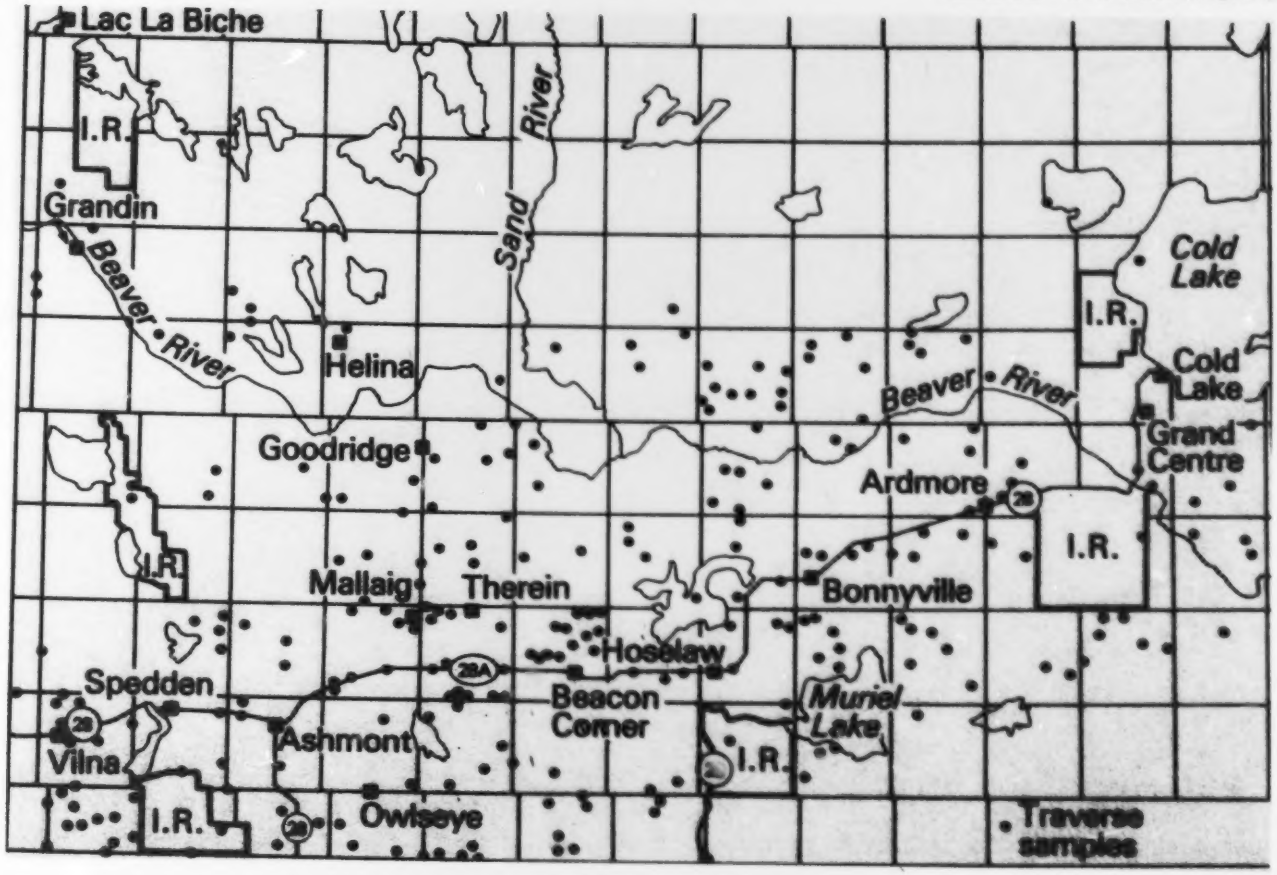
Spatial and temporal variations in

Groundwater chemistry of shallow aquifers in the Sand River area, Alberta

E.I. Wallick



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TERRAIN SCIENCES DEPARTMENT, ALBERTA RESEARCH COUNCIL
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Abstract

Groundwater samples from shallow (< 80 m) wells in the Sand River area (NTS 73L) were collected and chemically analyzed in August 1974 and in March 1975 to assess the magnitude of seasonal variation of groundwater composition. The samples were collected along a west-east traverse that essentially paralleled the regional topographic slope and the inferred regional groundwater flow direction. The means and standard deviations (frequency histograms) of the concentration differences (in mg/L) between summer and winter samplings were comparable in magnitude and showed that no statistical difference could be found between the two suites of samples. The variable shape and range of the frequency distributions, however, showed that a simple statistical averaging approach was not adequate as a way of interpreting the temporal variations. Where the frequency distributions were asymmetrical, as in the case of sodium, magnesium and chloride, the trend was for a higher summer than winter concentration. When the differences were plotted along the traverse, generally positive winter-summer concentration differences were found in drift and bedrock aquifers associated with the Wapiti Formation, while mainly negative shifts of the concentration differences were found in the thin drift aquifer underlain by the Lea Park Formation. Positive winter to summer shifts in the area of Wapiti Formation subcrop are likely the result of dilution and mixing. Negative shifts, on the other hand, were found primarily in the area underlain by the Lea Park Formation and were explained as due to flushing of salts from the soil and unsaturated zones during summer recharge. The groundwaters were very close to chemical equilibrium with respect to the minerals aragonite, calcite, dolomite, magnesite, siderite, amorphous silica and Ca-montmorillonite. These observations tend to support the belief that chemical variability of groundwater composition is constrained by equilibrium reactions with aquifer minerals. Carbonate and clay minerals appeared to be particularly important in controlling the composition because of the consistency of chemical equilibrium and the fact that these minerals are found everywhere in the drift and bedrock aquifers of the region.

Introduction

The spatial distribution of chemical constituents in groundwater is generally related to the flow pattern, mineralogical composition and climate of a groundwater basin. The fact that certain predictable changes in both the quality and quantity of dissolved matter take place during groundwater movement from areas of recharge to areas of discharge is useful in corroborating or refining the physical hydrogeological properties of a groundwater flow system. In general, the chemical composition of groundwater most closely resembles the weathering products of source materials in the recharge area, and the degree of mineralization increases exponentially with depth due to a decrease in flushing intensity, and laterally due to further dissolution of minerals along the flow path.

Temporal variations of groundwater chemistry reflect hydrogeochemical processes operating near the sampling point. Such processes can be both physico-chemical and biochemical, and the magnitude of variation in concentration of chemical constituents may be great enough to contribute uncertainty to the variability attributed to the spatial distribution. In this paper, the chemical variation between groundwater samples collected during winter and summer was a reasonable first attempt at documenting the phenomenon of temporal variation on a reconnaissance scale.[1]

This paper documents spatial and temporal variations in groundwater composition and shows how these variations relate to regional hydrogeological characteristics on a reconnaissance scale of 1:250 000. The role of solution-mineral equilibrium as a stabilizing influence on groundwater chemical composition is also considered.

The study area encompasses some 14 000 km² and is about 95 km northeast of Edmonton (see figure 1). The area lies entirely within the forested Interior Plains physiographic province. Highest elevations (about 860 m amsl) are found in the north-central part of the area;

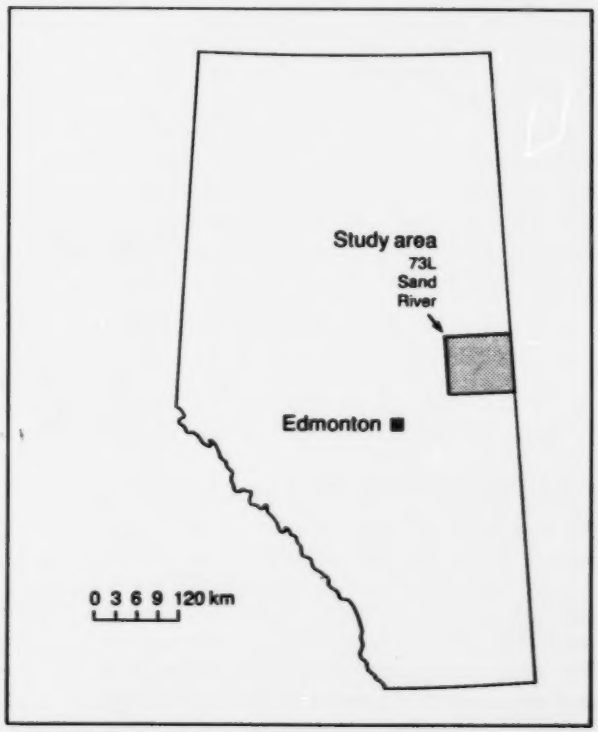


Figure 1. Location map.

[1]Davison and Vonhof (1978) have reported on groundwater chemical variations within an area of approximately 12 km² associated with a buried channel aquifer near Esterhazy, Saskatchewan. Samples were taken during November and June, July and August at intervals of one day.

the Beaver River valley at the point of juncture with the southeastern boundary of the area has an elevation of 490 m. Mean annual temperature is about 1°C, and the mean annual precipitation ranges from 363 to 620 mm. The area is almost entirely within the "short, cool summer" climatic zone (Ozoray *et al.*, 1980).

Physical hydrogeology

The most productive bedrock aquifer in the study area is the upper Cretaceous Wapiti Formation, but the lithologies alternate between lenticular montmorillonitic sandstones and clay shales, and the groundwater yields vary between 25 to 100 L/min. Generally, the glacial drift (consisting of sand, sand and silt or gravel, and till) is the most common shallow aquifer, and is characterized in most detail in this report. However, the variability of drift lithology and thickness (as little as 3 m in the southwest highland to more than 130 m in parts of buried valleys) is reflected in a range of yields from 5 to 25 L/min in some silt or till deposits to 450 to 2250 L/min in some sand and gravel lenses. The Lea Park Formation, also upper Cretaceous in age, is a poorly permeable marine clay-shale; it is the major bedrock aquitard in the area and the top of this formation essentially marks the lower limit of groundwater supplies in the area. Groundwater availability is very poor where the drift cover over the Lea Park is thin. The regional flow of groundwater is from west to east, and is essentially parallel to the trends of major streams and buried channels (Ozoray *et al.*, 1980).

Chemical hydrogeology

Acquisition of existing chemical data

Chemical analyses of groundwater sampled from wells in drift and shallow bedrock aquifers were obtained from the Central Data File of the Groundwater Department, Alberta Research Council. The analyses were, for the most part, the work of the Provincial Analyst and the Pollution Control Laboratory of Alberta Environment. The analyses were tested for internal precision by means of a cation-anion balance (where a complete analysis was given of major constituents) or a total dissolved solids (TDS) balance when determinations of sodium, potassium and separate analyses of calcium and magnesium were lacking. Of the 588 groundwater chemical analyses that were coded, 183 mainly partial analyses were rejected because error (ϵ) exceeded 20 percent for the TDS balance. The expression that was evaluated is written below:

$$\epsilon\ (\%) = \left[\frac{E_{cations} + E_{anions}{}^{*} - TDS}{TDS}\right] \times 100$$

$$^{*}E_{anions} = SO_4 + Cl + NO_3 + CO_3 + 0.49\ HCO_3$$

Field sampling and analysis

An additional 90 groundwater samples were first collected along Highway 28 from Vilna to Cold Lake in August 1974 and a second sampling of the same wells took place in March 1975. The path of the traverse and the distribution of wells sampled are shown on figure 2. The path cut across the area of greatest data density and was generally parallel to the regional west to east topographic slope in the southern half of the map area: from a high in the southwest of 670 masl near Vilna to a low at Cold Lake of 533 masl. Data of sufficient density for study were found only in the southern half of the map area and in the Lac La Biche Reserve. The traverse is also assumed to be parallel to any regional flow components.

The groundwater samples were collected from producing domestic wells after pumping until constant pH and temperature readings were obtained (usually within 15 minutes). Three 2-litre samples were collected in polyethylene bottles: one for field measurement of electrical conductivity, pH, alkalinity, iron content and temperature; a second acidized (drop by drop addition of concentration HNO_3 to pH <2.0) for

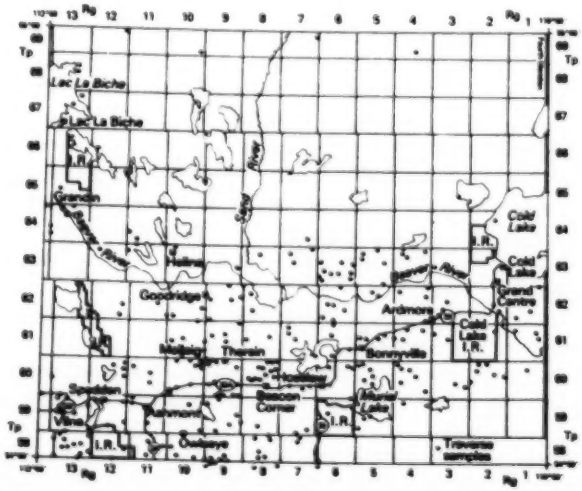


Figure 2. Distribution of sampling points.

analysis of total iron, calcium and magnesium contents; and a third for determination of major constituents. The latter two samples were analyzed using standard methods in the Geological Survey Chemistry Laboratory of the Alberta Research Council.

Measurement of field pH was carried out using an ORION model 401 meter and ORION 91-92 combination electrode. Buffers (pH = 7.00 and pH = 4.00) were refrigerated at about 10°C, a temperature approximating that of the groundwater. Alkalinity was determined by titrating 50 mL of water with 0.01647 N HCl to obtain pH versus volume of titrant added. The method of Barnes (1964) was employed to calculate the field alkalinity. Conductivity was measured using a Hach model 2510-01 conductivity meter. A Hach model 2504 spectrophotometer was used to analyze the total iron content by means of the 1,10 - Phenanthroline method. Temperature of the groundwater was measured with a glass mercury thermometer calibrated in 0.2°C intervals.

Results

General aspects of groundwater chemistry

High TDS (<1000 mg/L) are found in groundwater above or within the Wapiti Formation; groundwater from buried channel aquifers that overlie the Lea Park marine shale generally tends to be less than 1000 mg/L. Figure 3 shows these observations. Note that local pockets of either very poor (>2000 mg/L) or very fresh (<500 mg/L) groundwater occurs within the area.

As shown in figure 4, the most abundant chemical type of groundwater is a mixed type with neither bicarbonate nor sulfate type being dominant.[1] Regions of calcium-magnesium-bicarbonate groundwater mainly occur in the more productive drift aquifers. Calcium-sulfate and sodium-sulfate type groundwaters occur primarily in the southwestern portion of the area.

Groundwaters from the area are generally very low in chloride, although concentrations as high as 100 mg/L were found in the northwestern corner of the Cold Lake Indian Reserve. Near Goodridge, concentrations as high as 70 mg/L were noted. Chloride concentrations are generally well below 50 mg/L elsewhere in the Sand River area, and are especially low in aquifers associated with the Wapiti Formation and the preglacial channels, presumably due to active circulation of groundwater.

The distribution of groundwater chemical types with respect to depth can be portrayed by a modified Piper diagram (Piper, 1944). The mean depth of the open interval is plotted in the water-type field in figure 5. The figure shows that calcium-magnesium-bicarbonate waters predominate at depths less than 30 m, although other water types still appear in this depth zone. Calcium-magnesium-sulfate type groundwater is generally found at depths less than 45 m. Sodium-sulfate type of groundwater tends to occur in deeper wells. The trend indicates the groundwaters change from calcium-magnesium-bicarbonate facies to sodium-sulfate facies with increasing depth.

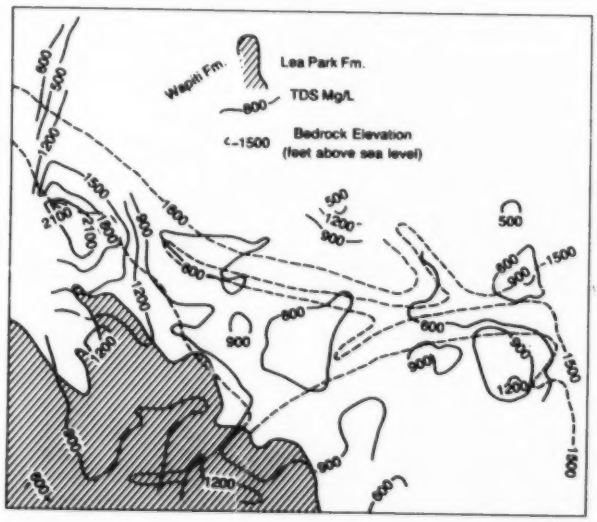


Figure 3. Distribution of total dissolved solids, geology and topography of the bedrock surface.

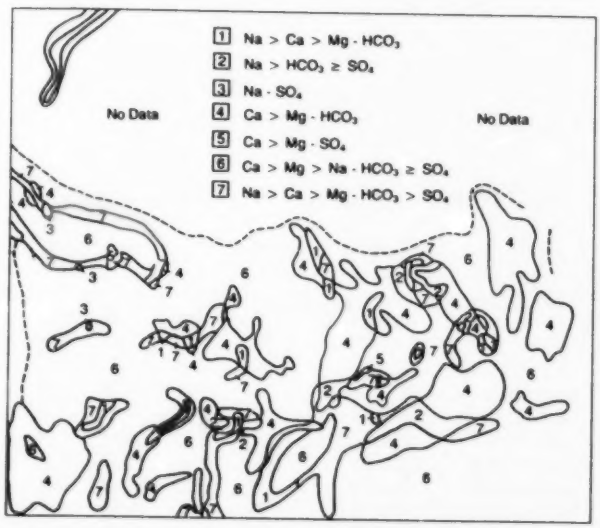


Figure 4. Distribution of groundwater chemical types.

[1]That is, greater than 60% of total anions.

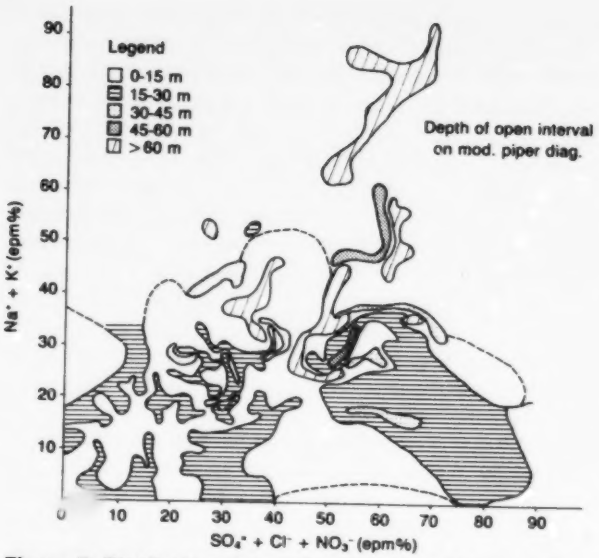


Figure 5. Distribution of groundwater chemical types with respect to depth.

Results of field study

Table 1 summarizes the results of the field and laboratory chemical analyses. Chemical analyses of major and minor constituents were performed in the Geological Survey Chemistry Laboratory, under the supervision of J.R. Nelson, within two or three weeks after sampling. The symbols, Ca_T^{++} and Mg_T^{++} are the concentrations of calcium and magnesium respectively in the acidified samples. The adjusted bicarbonate concentration, HCO_{3T}, takes the precipitation of calcite between times of sampling and analysis into account (Wallick, 1977). The table gives the results of summer and winter sampling.

Some observations concerning the magnitude and variation of the chemical parameters may be made:

Differences between the concentrations of various constituents from winter and summer samplings are expressed as frequency histograms (figure 6 a-h). In all cases, the mean is not significantly different from zero, indicating no clear difference between winter and summer groundwater composition. However, the variable shapes and ranges of the frequency histograms reflect an aspect of the chemical variability that is not explained by a simple statistical averaging approach. For example, $\Delta[Ca^{++}]$ is distributed more or less symmetrically about zero as a bell-shaped normal distribution. Δ $[Na^+]$, however, is not symmetrically distributed, but skewed toward negative differences. Examination of the remaining distributions shows that $\Delta[HCO_3^-]$, $\Delta[SO_4^{--}]$, $\Delta[NO_3^-]$, and ΔTDS are normal, while $\Delta[Mg^{++}]$ and $\Delta[Cl^-]$ are skewed. The sodium, magnesium and chloride distributions are skewed in the direction of higher summer than winter concentrations.

Another way of looking at the differences is to consider their variation with distance along the traverse. Figure 7 (a-h) shows the differences expressed as a percent of the summer concentration. The diagrams demonstrate the relative importance of the variations, showing that in excess of 100 percent variation in Na^+ can be obtained and more than 50 percent variation in Ca^{++} and Mg^{++} occurred. With respect to anions, the variation in HCO_3^- was usually less than 50 percent, $[Cl^-]$ showed large percentage variation (in excess of 100 percent for positive shifts and on the order of 50 percent for negative shifts), and $[SO_4^{--}]$ and $[NO_3^-]$ showed similarly large variations.

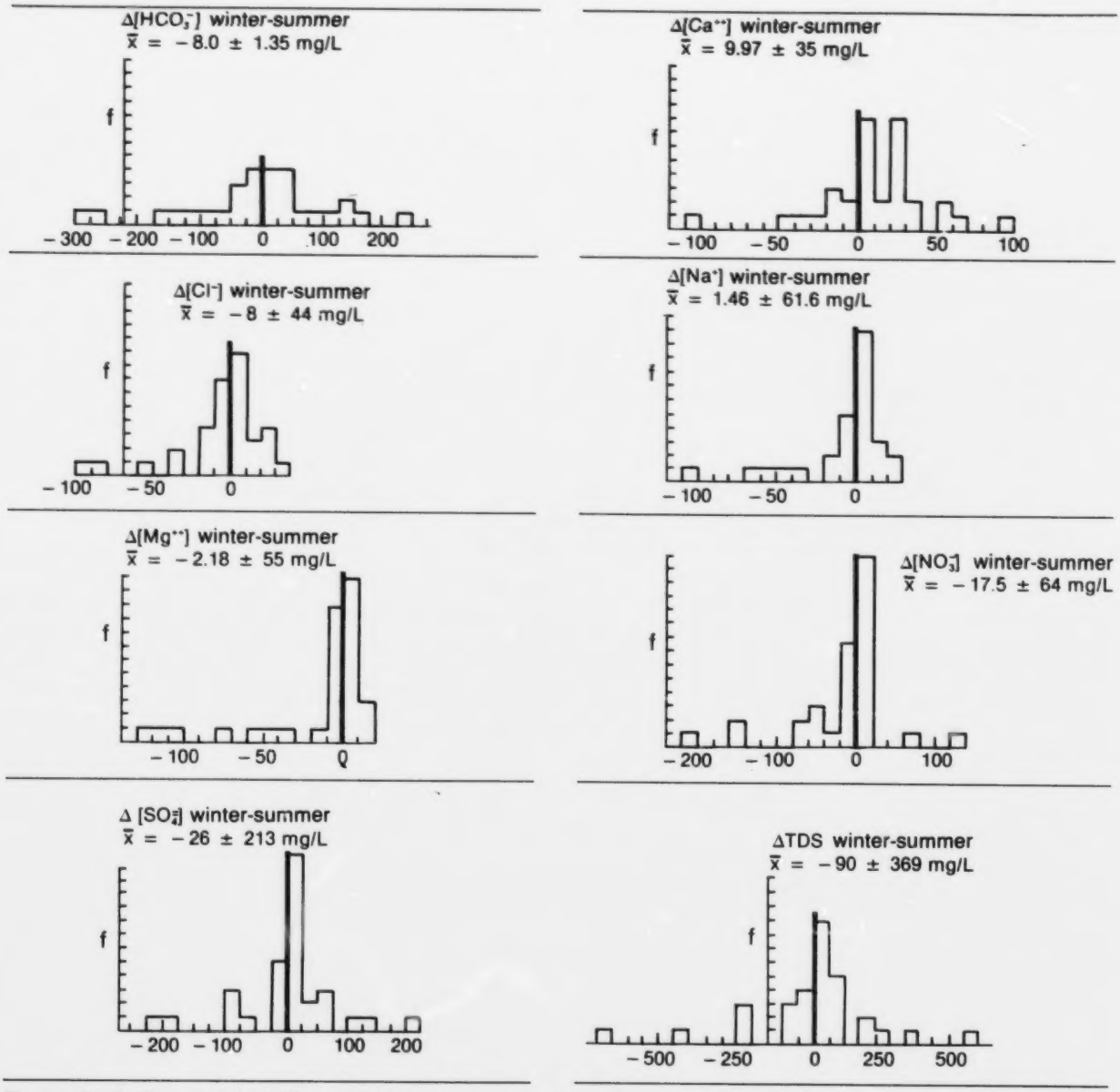
Plotting these variations along the traverse is a simple means of checking whether the differences are randomly distributed in space. They are not. Positive deflections of Na^+, Mg^{++} and SO_4^{--} tend to occur along the west half of the traverse while negative deflections tend to occur along the east half. Variations of Cl^- and NO_3^- generally tend to be uniform along the traverse.

Table 1. Chemical analyses of groundwater samples, Sand River (73L)

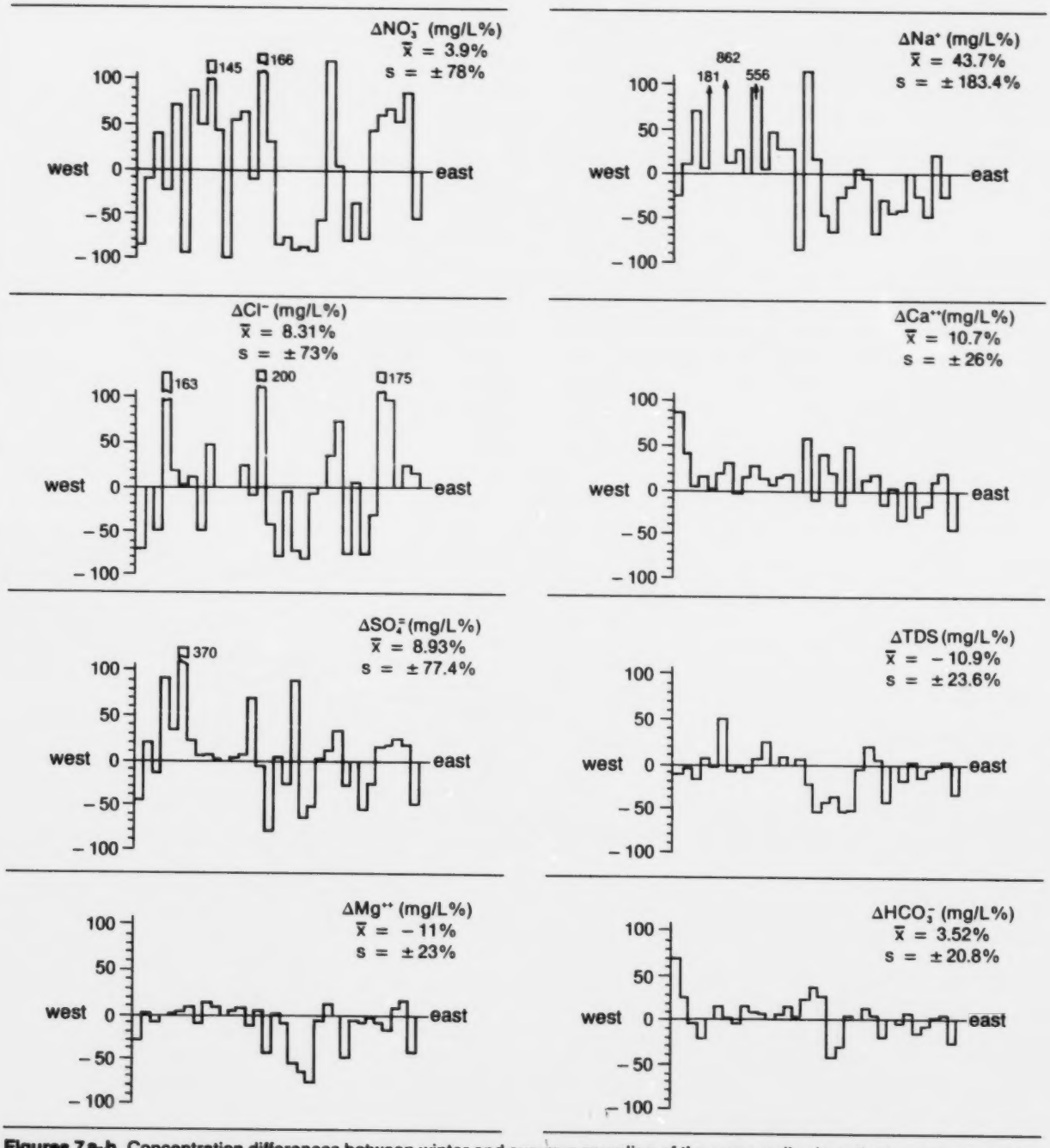
Location	Date	Depth	Temp	pH_f	pH_L	Cond	Ca^{++}	Ca^{++}_T	Mg^{++}	Mg^{++}	Na^+	K^+	CO_3	$HCO_3^-{}_T$
4-61-6-14-1	24/8/74	4.3	8.89	7.50	8.20	1150	73.0	108.7	73.5	82.8	16.3	3.3	-	512.6
4-61-6-14-1	25/3/75	4.3	9.00	7.10	7.50	990	102.0	113.3	67.0	71.1	18.8	3.3	-	654.0
4-61-5-22-13	25/8/74	5.5	12.22	7.32	8.00	2700	116.0	142.9	300.0	300.0	78.8	5.0	-	1022.7
4-61-5-22-13	24/3/75	5.5	3.50	7.30	7.60	1610	137.0	166.7	137.0	133.3	41.3	9.6	-	576.0
4-61-5-26-12	25/8/74	6.7	1.22	7.12	8.00	2000	119.2	156.2	195.0	194.4	89.0	5.8	-	905.5
4-61-5-26-12	25/3/75	6.7	7.00	7.20	7.40	1025	100.0	114.4	63.0	67.8	27.5	5.8	-	625.0
4-61-5-25-1	25/8/74	30.5	8.33	7.35	7.90	4000	279.0	322.7	325.0	350.0	399.0	8.3	-	571.1
4-61-5-25-1	24/3/75	30.5	8.80	7.30	7.80	2600	187.0	221.1	78.0	80.0	289.0	8.8	-	596.0
4-61-4-32-1	25/8/74	9.8	8.89	7.32	8.20	1000	77.7	77.0	66.0	64.4	64.0	3.3	-	617.5
4-61-4-32-1	24/3/75	9.8	4.00	7.30	7.60	980	76.0	88.9	63.0	67.8	55.0	4.6	-	615.0
4-62-4-2-8	25/8/74	8.5	9.44	7.30	7.60	850	87.6	91.3	56.0	57.2	11.0	2.9	-	524.8
4-62-4-2-8	24/3/75	8.5	-	7.30	7.50	940	96.0	106.9	64.0	66.7	11.3	4.2	-	586.0
4-63-2-24-9	26/8/74	17.1	11.66	7.03	7.80	1700	172.6	186.2	99.5	95.6	109.0	6.3	-	588.2
4-63-2-24-9	24/3/75	17.1	11.00	6.90	7.30	1880	199.0	225.6	99.0	104.4	105.0	9.2	-	615.0

Table 1. Chemical analyses of groundwater samples, Sand River (73L) (cont'd)

Location	Date	Depth	Temp	pH_f	pH_L	Cond	Ca^{++}	Ca^{++}_T	Mg^{++}	Mg^{++}_T	Na^+	K^+	CO_3	HCO_3^-
4-63-2-15-1	26/8/74	12.2	8.33	7.50	7.90	1575	130.0	127.8	108.5	103.9	81.0	3.8	-	624.8
4-63-2-15-1	24/3/75	12.2	3.80	7.10	7.70	965	110.0	124.4	56.0	58.9	25.0	5.8	-	493.0
4-62-2-35-15	26/3/74	11.4	8.89	7.07	8.00	1000	101.8	113.1	51.0	47.2	34.0	6.7	-	449.1
4-62-2-35-15	24/3/75	11.4	5.50	6.90	7.30	815	105.0	123.3	48.0	53.3	23.8	7.9	-	454.0
4-62-2-36-14	26/3/74	9.1	14.44	7.18	8.00	1100	154.8	152.0	52.0	52.2	14.0	4.2	-	546.7
4-62-2-36-14	24/3/75	9.1	5.50	7.00	7.40	825	106.0	117.8	47.5	50.0	7.5	1.7	-	527.0
4-62-1-31-15	26/8/74	7.3	8.89	7.23	8.30	8.50	92.8	96.4	48.5	48.9	11.0	5.4	-	468.6
4-62-1-31-15	24/3/75	7.3	7.30	7.10	7.50	870	101.0	111.1	47.5	53.3	6.3	5.0	-	503.0
4-63-1-2-2	26/8/74	7.6	6.11	7.20	7.40	950	122.2	129.6	50.0	50.0	5.0	2.9	-	566.3
4-63-1-2-2	24/3/75	7.6	9.00	7.40	8.10	875	88.0	124.4	45.6	46.7	5.0	10.4	-	464.0
4-62-2-22-16	27/8/74	29.0	9.44	7.20	7.80	1100	133.2	136.0	57.5	55.0	54.0	5.0	-	663.9
4-62-2-22-16	24/3/75	29.0	4.70	71.0	8.20	1120	111.0	136.7	55.0	56.7	40.0	2.9	-	605.0
4-62-2-23-4	27/8/74	11.6	8.89	6.97	7.60	1100	159.8	166.7	55.5	57.8	15.0	63.	-	541.9
4-62-2-23-4	24/3/75	11.6	6.00	7.00	7.20	1110	174.0	193.3	53.0	55.6	7.5	5.8	-	542.0
4-62-2-14-5	27/8/74	10.4	14.44	6.91	7.90	875	113.4	129.1	38.5	40.0	15.0	7.0	-	488.2
4-62-2-14-5	24/3/75	10.4	11.0	6.90	7.30	910	134.0	145.6	39.7	42.2	8.8	6.3	-	517.0
4-62-3-8-13	27/5/74	5.5	6.11	7.07	7.60	3300	253.3	261.7	178.0	166.7	356.0	4.6	-	868.9
4-62-3-8-13	24/3/75	5.5	4.50	7.10	7.80	2500	148.0	208.9	107.0	107.8	258.0	5.4	-	615.0
4-59-13-20-1	21/8/74	15.2	3.89	7.40	8.10	1600	63.7	158.3	68.0	69.9	68.8	22.9	-	361.2
4-59-13-20-1	26/3/75	15.2	1.30	7.30	7.60	1050	119.0	136.7	48.5	50.0	52.5	6.3	-	608.0
4-59-13-20-5	21/8/74	39.6	2.22	7.40	8.10	1400	98.4	129.6	53.0	54.4	55.0	4.6	-	478.4
4-59-13-22-5	26/3/75	39.6	4.50	7.30	7.50	1210	138.0	158.9	54.0	57.8	61.0	5.0	-	603.0
4-59-13-22-5	21/8/74	42.7	4.44	7.48	7.80	900	89.5	96.0	38.5	41.1	18.8	6.7	-	466.2
4-59-13-33-5	26/3/75	42.7	3.00	7.30	7.60	790	93.0	106.7	35.0	38.9	23.8	6.7	-	454.0
4-59-13-33-2	22/8/74	5.2	13.88	7.02	7.70	1100	155.4	161.1	61.5	64.4	8.8	3.3	-	732.2
4-59-12-32-2	23/6/75	5.2	6.80	7.00	7.30	1300	180.0	203.3	62.0	63.3	15.0	7.1	-	571.0
4-59-12-33-1	22/5/74	30.5	9.44	7.20	7.60	1450	170.3	180.9	64.5	64.9	98.8	6.3	-	639.5
4-59-12-33-1	25/3/75	30.5	5.70	7.20	7.60	1550	173.0	196.7	66.0	68.9	104.0	6.7	-	644.0
4-59-11-28-12	22/8/74	24.4	6.10	7.29	7.70	1550	156.0	158.1	106.0	111.1	16.5	6.7	-	656.6
4-59-11-28-12	25/3/75	24.4	2.60	7.10	7.40	1820	214.0	243.3	103.0	106.7	46.3	6.7	-	561.0
4-59-11-30-16	22/8/74	15.2	6.70	7.35	7.80	1000	110.8	115.1	54.5	57.8	1.3	5.8	-	556.5
4-59-11-30-16	25/3/75	15.2	4.50	7.20	7.50	990	144.0	215.6	59.0	76.7	12.5	10.0	-	564.0
4-59-11-28-16	22/8/74	35.4	7.20	7.22	7.60	1850	185.0	203.1	78.0	82.2	10.13	5.4	-	676.1
4-59-11-28-16	25/3/75	35.4	2.50	7.30	7.50	1700	182.0	133.3	71.0	60.0	113.0	5.4	-	639.0
4-60-10-8-8	22/8/74	8.5	6.10	7.18	7.50	1700	197.0	221.7	108.0	108.9	28.8	6.3	-	693.0
4-60-10-8-4	25/3/75	8.5	3.40	7.20	7.70	1925	220.0	253.3	124.0	115.6	36.3	6.7	-	800.0
4-60-10-25-1	23/8/74	76.2	7.80	7.57	8.10	2150	72.6	88.9	28.5	30.0	431.0	5.0	-	551.6
4-60-10-25-1	25/3/75	76.2	5.00	7.50	7.70	2500	93.0	104.4	31.0	32.2	426.0	5.4	-	600.0
4-60-9-17-2	24/8/74	12.2	7.20	7.46	8.20	600	63.8	69.2	25.0	26.7	5.0	2.5	-	346.6
4-60-9-17-2	25/3/75	12.2	5.00	7.30	7.70	625	71.0	78.9	25.0	26.7	283.0	3.8	-	371.0
4-60-9-13-12	24/8/74	59.7	7.20	7.80	8.20	2075	39.2	42.3	16.0	15.6	427.5	2.9	-	634.6
4-60-9-13-12	25/3/75	59.7	3.80	7.70	7.60	2020	42.0	56.7	16.8	16.7	444.0	4.6	-	637.0
4-60-5-16-4	24/5/74	16.5	6.10	7.11	7.60	1700	145.0	143.3	128.0	137.8	18.8	4.2	-	595.6
4-60-5-16-4	25/3/75	16.5	4.50	7.20	7.20	1880	164.0	162.0	139.0	147.0	27.5	4.6	-	639.0
4-60-7-17-1	24/5/74	12.2	8.90	7.10	7.90	1650	139.0	178.9	105.0	108.3	30.0	5.0	-	532.1
4-60-7-17-1	25/3/75	12.2	7.50	7.10	7.30	1550	161.0	168.9	92.0	102.2	37.5	5.4	-	610.0
4-60-7-12-15	24/8/74	10.0	6.10	7.25	7.80	1100	120.0	128.8	48.0	51.1	28.8	5.0	-	649.3
4-60-7-12-16	25/3/75	10.1	3.80	7.10	7.30	1040	120.0	144.4	51.0	55.6	36.3	5.0	-	676.0
4-60-6-16-7	24/8/74	30.0	8.90	7.21	7.80	1700	102.7	150.6	110.0	124.4	56.3	5.8	-	561.4
4-60-6-16-9	28/5/74	30.0	4.80	7.00	7.30	1210	163.0	185.6	64.0	65.6	6.3	9.6	-	698.0
4-60-6-35-13	24/5/74	5.5	5.60	7.15	7.90	1200	107.0	136.9	47.5	52.8	22.5	6.7	-	451.5
4-60-6-35-13	25/3/75	5.5	2.30	7.20	7.60	925	96.0	115.6	48.0	53.3	48.8	4.2	-	617.0



Figures 6 a-h. Concentration differences between winter and summer sampling of the same wells, expressed in frequency histograms.



Figures 7 a-h. Concentration differences between winter and summer sampling of the same wells along the traverse, expressed as mg/L percent.

Discussion

The point where the traverse crosses the contact between the Wapiti Formation and the Lea Park Formation is indicated on figures 7 (a-h) by a vertical line. It may be noted that this point correlates with the changes noted in the previous section pertaining to positive versus negative percentage differences. On figure 3, a contour map of TDS is superimposed upon a map giving the contact between the Belly River and Lea Park Formations and the bedrock topography. Note that the TDS are significantly higher in groundwater obtained from aquifers in the area of Wapiti Formation subcrop compared to the TDS from aquifers

overlying the Lea Park Formation. This difference occurs for the following reasons: the aquifer thickness and permeability are greater in the area underlain by the Wapiti Formation than in the area underlain by the Lea Park, where the aquifers are thin drift sands and channel sands and gravels resting on very poorly permeable marine clay-shale. Therefore, deeper flow systems with longer groundwater residence times and greater groundwater mineralization can develop in the area associated with the Wapiti Formation.

Positive winter-summer concentration differences in aquifers associated with the drift and bedrock in the area of Wapiti Formation subcrop may also be expected because of the effects of dilution and mixing as a result of groundwater recharge. On the other hand, negative fluctuations of the percentage concentration differences in the thin drift aquifer underlain by the Lea Park (see particularly figure 7) can be explained by flushing of salts from the soil and unsaturated zones during summer recharge. The total volume of groundwater in storage in the thin drift aquifer, which is significantly less than the volume stored in the thicker drift and bedrock aquifer associated with the Wapiti Formation, suggests that the effect of flushing of salts would be accentuated in aquifers overlying the Lea Park. The *relative* effect of any dilution or flushing event would appear greater in aquifers that are of small storage capacity because of the greater proportion of added salt or water to that already in storage.

Control of solubility by minerals

Whereas the time and spatial variability of the chemical concentrations in groundwater are increased by mixing and flushing, equilibrium controls on solubility by aquifer minerals tend to stablize the concentrations. It is useful, therefore, to determine the disequilibrium index distribution with respect to various minerals present in the drift and bedrock of the Sand River area.

Relation of hydrochemistry to aquifer mineralogy

The disequilibrium index was defined by Paces (1972) as the log of the ratio of the activity product to the temperature-corrected equilibrium constant:

$$I = \log (Q/K_T)$$

For example, in the case of gypsum dissolved in pure water, the chemical reaction would be

$$CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{++} + SO_4^{=} + 2H_2O$$

The activity product for the above reaction is

$$Q = \frac{(Ca^{++})(SO_4^{=})}{(CaSO_4)}$$

where ( ) = free ion activity

If the solution were undersaturated or oversaturated, the value of I would be less than or greater than ± 0.5 respectively (Paces, 1972). Water samples that are saturated, or in equilibrium with a given mineral, are assumed to have been in contact with that mineral prior to pumping or spring discharge.

Disequilibrium indices with respect to calcite, dolomite, gypsum, Ca-montmorillonite, illite, kaolinite, albite, anorthite and microcline were computed by means of a simple computer program. The program calculates the equilibrium-free ion activities of Ca^{++}, Mg^{++}, Na^{+}, K^{+}, H^{+}, $SO_4^{=}$, H_2CO_3, HCO_3^{-}, $CO_3^{=}$, Cl^{-} and P_{CO_2} (atm.) by iteratively forming the ion pairs: $CaSO_4$, $NaSO_4^{-}$, $MgSO_4$ and $CaCO_3$. Input to the program consists of the field pH and temperature, and bicarbonate/carbonate concentration(s) measured in the field or reconstructed from suitable laboratory data (Wallick, 1977), Ca^{++} and Mg^{++} measured on an acidified portion of the groundwater sample, and analyses for $SO_4^{=}$, CL^{-}, NO_3^{-}, H_4SiO_4, F^{-}, and total iron measured on the acidified sample or the equivalent analysis in the field. The program was used to compute disequilibrium indices for samples collected in 1974.

SOLMNEQ (Kharaka and Barnes, 1973), the solution mineral equilibrium program, was used to compute disequilibrium indices for laboratory and field chemical states of all samples taken in 1974 and 1975. Values of I for the minerals aragonite, calcite, dolomite, gypsum, magnesite, siderite and amorphous silica were closest to saturation from among 157 mineral species treated in the program.

Data from both computer calculations are summarized in table 2. Assuming the $-0.5 \leq I \leq +0.5$ criterion to denote equilibrium conditions, the groundwater was, on the average, in equilibrium with calcite, aragonite, dolomite, magnesite, siderite, amorphous silica and Ca-montmorillonite. Of interest are the differences in index values between field and laboratory chemical states for the carbonate minerals. (The laboratory chemical state is the chemical analysis of the non-acidified sample at ~25°C and includes the laboratory pH.) In all cases (except siderite), there is a shift from a saturated to an oversaturated state. The primary reason for this is the loss of dissolved CO_2 from warming the sample. For instance, the average partial pressures of CO_2, P_{CO_2}, calculated using SOLMNEQ, were as follows:

a. P_{CO_2} (field samples August/74) = $(3.13 \pm 1.89) \times 10^{-2}$ atm
b. P_{CO_2} (field samples March/75) = $(2.97 \pm 1.29) \times 10^{-2}$ atm
c. P_{CO_2} (field all samples) = $(3.08 \pm 1.22) \times 10^{-2}$ atm
d. P_{CO_2} (lab all samples) = $(1.28 \pm .52) \times 10^{-2}$ atm

These data show that the equilibrium partial pressure of CO_2 is constant under field conditions from summer to winter, but that more than 50 percent of the CO_2 escapes by the time the sample is analyzed in the laboratory. Table 2 further documents the effect of CO_2 loss by sample warming. Note how close to saturation

(0 within ± 0.5) the groundwaters were in the field with respect to the carbonate minerals: calcite, aragonite, dolomite, siderite and magnesite; and how, in the laboratory state, the waters were oversaturated. In general, the Sand River area groundwaters analyzed for this report were in equilibrium with carbonate minerals in the field. The values for gypsum in the field and in the laboratory are identical because no loss of $SO_4^{=}$ occurs during sample warming.

With regard to the silicate minerals, the groundwaters were in equilibrium with amorphous silica and Ca-montmorillonite, slightly oversaturated with respect to kaolinite, undersaturated with respect to illite, microcline and albite, and greatly undersaturated with respect to anorthite.

Another way of interpreting the results pertaining to the silicate minerals in table 2 is the aspect of mineral stability in the aquifer. The more negative the value for I, the less stable a particular mineral is when in contact with the specified groundwater composition. Anorthite

Table 2. Disequilibrium indices, Sand River (73L)

	I	± s	N	Program	State
Calcite ($CaCO_3$)	0.25	0.16	54	W	F
	0.17	0.13	88	S	F
	0.89	0.17	88	S	L
Aragonite ($CaCO_3$)	0.14	0.13	88	S	L
	0.78	0.17	88	S	L
Dolomite ($CaMg(CO_3)_2$)	0.51	0.37	54	W	F
	0.37	0.52	87	S	F
	1.70	0.67	87	S	L
Siderite ($FeCO_3$)	0.12	0.38	56	S	F
	No laboratory calculation possible because iron precipitates from solution.				
Gypsum ($CaSO_4$ $2H_2O$)	-1.46	0.49	54	W	F
	-1.21	0.41	89	S	F
	-1.22	0.39	87	S	L
Magnesite ($MgCO_3$)	-0.21	0.20	89	S	F
	0.46	0.21	89	S	L
Amorphous silica	-0.12	0.06	88	S	F
	-0.24	0.06	85	S	L
Ca-montmorillonite	0.92	0.10	54	W	F
Illite	-0.73	0.20	54	W	F
Kaolinite	0.92	0.16	54	W	F
Microcline	-1.49	0.27	54	W	F
Albite	-2.74	0.60	54	W	F
Anorthite	-10.79	0.31	54	W	F

N = Number of samples
F = Field
L = Laboratory
W = Equilibrium computer model PHCALC
S = SOLMNEQ

is, therefore, the least stable mineral in the table, and Ca-montmorillonite is the most stable mineral.

The following minerals are probably present in the drift based on x-ray diffraction analysis of drift samples over the same bedrock unit (Belly River Formation) approximately 300 km (100 mi) south of the Sand River area: quartz, plagioclase, dolomite, calcite, very minor gypsum, montmorillonite, illite, kaolinite (Wallick, 1981). The results of the chemical equilibrium computations tend to support the belief that chemical variability of groundwater composition is constrained by equilibrium reactions with the aquifer mineral assemblage. The carbonate and clay minerals seem particularly important in controlling composition because the values of I obtained were closest to zero.

Summary and conclusions

The general hydrochemistry of shallow groundwater in the Sand River area is characterized by TDS < 1000 mg/L in groundwater from aquifers that overlie the Lea Park marine shale, while TDS values generally exceed 1000 mg/L in groundwater from aquifers associated with the Wapiti Formation. The differences in chemical composition between winter and summer samplings of the same wells plotted on frequency histograms show that although the mean differences were statistically indistinguishable from zero, the distributions of sodium, magnesium and chloride were skewed in the direction of higher summer than winter concentrations. This was attributed to flushing of these highly mobile cations from the soil and unsaturated zone during spring and summer infiltration. When the concentration differences of major chemical constituents were plotted as a non-scalar bar graph along the traverse, positive deflections in Na, Mg, Ca and SO_4 percentage concentration differences tended to occur in aquifers on the western half underlain by the Wapiti Formation. Negative deflections tended to occur in aquifers in the eastern half underlain by the Lea Park Formation. These observations were explained by noting that the groundwater flow systems developed in the area where the Wapiti Formation subcrops are deeper and have a longer residence time so that groundwater can become more mineralized. The relative effect of flushing of salts and groundwater mixing on chemical variability would be less in aquifers associated with the Wapiti Formation compared to those underlain by the Lea Park Formation because of the greater amount of groundwater in storage in the Wapiti Formation.

Examination of the disequilibrium indices, computed by means of PHCALC and SOLMNEQ, showed that carbonate and clay minerals were the most important solid phases entering into chemical equilibrium with the groundwater. Chemical equilibrium is believed to be a stabilizing influence on groundwater composition.

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Appendix PHCALC Interactive Computer

Model for obtaining equilibrium pH, PCO_2, and disequilibrium indices

```
      DATA AMEN,A1M,A2M,A3P,AMEN,A1M,A2M,A3P,A4,A-/
     13.719E-2,4.16E-7,4.94E-11,4.59E-9,-4.6312E3,
     21.82E3,3.99E3,-2.89E3,1.E-14,1.338E6/
      TEMPCO(A,B,C)=A+(B-298.)/(5*298.*1.987)+ALOG(C)
100   WRITE(2,2)
2     FORMAT(1X,$PROGRAM PHCALC IS READY FOR USE$,
     1/,1X,$ENTER DATA AS REQUIRED.$)
      WRITE(6,101)
101   FORMAT(1H1)
      WRITE(2,22)
22    FORMAT(/,1X,$INDEX NO.=$,1X)
      READ(1,222) SAMPLE
222   FORMAT(2A8)
      WRITE(2,33)
33    FORMAT(/,1X,$CALCIUM(PPM)=$,1X)
      READ(1,4) SCA
4     FORMAT(F10.2)
      WRITE(2,5)
5     FORMAT(/,1X,$MAGNESIUM(PPM)=$,1X)
      READ(1,4) SMG
      WRITE(2,6)
6     FORMAT(/,1X,$SODIUM(PPM)=$,1X)
      READ(1,4) SNA
      WRITE(2,7)
7     FORMAT(/,1X,$POTASSIUM(PPM)=$,1X)
      READ(1,4) SK
      WRITE(2,8)
8     FORMAT(/,1X,$CHLORIDE(PPM)=$,1X)
      READ(1,4) SCL
      WRITE(2,9)
9     FORMAT(/,1X,$SULFATE(PPM)=$,1X)
      READ(1,4) SSO4
      WRITE(2,10)
10    FORMAT(/,1X,$CARBONATE(PPM)=$,1X)
      READ(1,4) SCO3
      WRITE(2,11)
11    FORMAT(/,1X,$BICARBONATE(PPM)=$,1X)
      READ(1,4) SHCO3
      WRITE(2,115)
115   FORMAT(/,1X,$NO3(PPM)=$,1X)
      READ(1,4) SNO3
      WRITE(2,116)
116   FORMAT(/,1X,$SIO2(PPM)=$,1X)
      READ(1,4) SIO2
      WRITE(2,12)
12    FORMAT(/,1X,$FIELD TEMP. (DEG F) =$,1X)
      READ(1,4) TEMP
      XTEMP=0.5555*(TEMP-32.)
      WRITE(2,13)
13    FORMAT(/,1X,$FIELD PH=$,1X)
      READ(1,4) PH
      WRITE(6,393) SAMPLE,SCA,SMG,SNA,SK,SCL,SSO4,SCO3,SHCO3,SNO3
     1,SIO2,XTEMP,PH
393   FORMAT(/,30X,$INPUT DATA ECHO$,//,$SAMPLE=$,2A8,2X,$CA=$,
     1F7.2,2X,$MG=$,F7.2,2X,$NA=$,F7.2,2X,$K=$,F7.2,/,1X,
     1$CL=$,F7.2,2X,$SO4=$,F7.2,2X,$CO3=$,F7.2,2X,$HCO3=$,
     1F7.2,2X,$NO3=$,F7.2,/,1X,$SIO2=$,F7.2,2X,$T(C)=$,F7.2,
     12X,$PH(FIELD)=$,F7.2)
      ZCA=SCA/40.08E3
      ZMG=SMG/24.32E3
      ZNA=SNA/22.991E3
      ZK=SK/39.102E3
      ZCL=SCL/35.457E3
      ZSO4=SSO4/95.86E3
      ZCO3=SCO3/60.E3
      ZHCO3=SHCO3/61.E3
      ZNO3=SNO3/62.E3
      ZSIO2=SIO2/60.09E3
      BTEMP=XTEMP+273.
      BMEN=EXP(TEMPCO(AMEN,BTEMP,AMEN))
      B1M=EXP(TEMPCO(A1M,BTEMP,A1M))
      B2M=EXP(TEMPCO(A2M,BTEMP,A2M))
      BW=EXP(TEMPCO(AW,BTEMP,AW))
      B3P=EXP(TEMPCO(A3P,BTEMP,A3P))
      ACT1=4.9
      ACT2=8.7
      ZCACO3=ZMGSO=ZNASO=ZCASO=0.
      ZCACO=B3P/6.E-4
      ZCA=ZCA-ZCACO
      OH=14.-PH
      ZOH=10.**(-OH)
      ZH=10.**(-PH)
      ZCO3=(B2H*ZHCO3)/(ACT2+ZH)
      K1=0
3     XCA=ZCA
C     CALCULATE IONIC STRENGTH
      U=0.5*(2.*(ZCA+ZMG+ZSO4+ZCO3)+2.5*(ZNA+ZK+ZCL
     1+ZHCO3+ZNO3+ZOH+ZH+ZNASO))
      EX=-0.509*U/(1.0+1.3*U)
C     CALCULATE ACTIVITY COEFFICIENT FOR MONOVAL. IONS
      ACT1=10.**EX
C     CALCULATE ACTIVITY COEFFICIENT FOR DIVAL. IONS
      EX=EX*4.
      ACT2=10.**EX
C     TREATMENT OF MAGNESIUM SULFATE ION PAIR
      IF(ZSO4)796,796,791
791   IF(ZMG)796,796,792
792   AA=ACT2**2
      BB=-(5.9E-3+AA*ZMG+AA*ZSO4)
      CC=AA*ZMG*ZSO4-5.9E-3*ZMGSO
      XXXX=BB*BB-4.0*AA*CC
      IF(XXXX)793,793,794
793   X3=0.0
      GO TO 795
794   X3=(-BB-SQRT(XXXX))/(2.0*AA)
795   ZMGSO=ZMGSO+X3
      ZMG=ZMG-X3
      ZSO4=ZSO4-X3
C     TREATMENT OF CALCIUM SULFATE ION PAIR
796   IF(ZSO4)296,296,291
291   IF(ZCA)296,296,292
292   AA=ACT2**2
      BB=-(4.9E-3+AA*ZCA+AA*ZSO4)
      CC=AA*ZCA*ZSO4-4.9E-3*ZCASO
      XXXX=BB*BB-4.0*AA*CC
      IF(XXXX)293,293,294
293   X4=0.
      GO TO 295
294   X4=(-BB-SQRT(XXXX))/(2.0*AA)
295   ZCASO=ZCASO+X4
      ZCA=ZCA-X4
      ZSO4=ZSO4-X4
C     TREATMENT OF SODIUM SULFATE ION PAIR
295   IF(ZSO4)396,395,391
391   IF(ZNA)396,395,392
392   AA=ACT2
      BB=-(1.9E-1+AA*ZNA+AA*ZSO4)
      CC=AA*ZNA*ZSO4-1.9E-1*ZNASO
      XXXX=BB*BB-4.0*AA*CC
      IF(XXXX)393,393,394
393   X5=0.
      GO TO 395
394   X5=(-BB-SQRT(XXXX))/(2.0*AA)
395   ZNASO=ZNASO+X5
      ZNA=ZNA-X5
      ZSO4=ZSO4-X5
C     TEST IF CALCIUM CONCENTRATION IS CONSTANT
396   K1=K1+1
      ERROR=(XCA-ZCA)/XCA
      IF(ABS(ERROR).GT..01) GO TO 3
      ZH=ZH/ACT1
      EQPH=(B2H/B3P)*ZCA*ZHCO3**ACT2
      EQPH=-ALOG10(EQPH**ACT1)
      SIC=ALOG10((ACT2*ZCA+ZHCO3+B2H*10.**(-PH))/B3P)
      SID=ALOG10((ACT2*ACT2*ACT1*ACT1*ZCA*ZMG*ZHCO3*ZHCO3
     1*B2H*B2H*10.**(2.*PH))/2.34E-17)
      SIG=ALOG10(ZCA*ZSO4*ACT2*ACT2)+4.61-2.49E-3*XTEMP+
     15.92E-5*XTEMP*XTEMP
      ZCO2=B3P/(ZCA*(ACT2*ACT2))
      ZHCO3=(ZH*ACT2*ZCO3)/B2M
      ZH2CO3=(ZH*ZHCO3*(ACT1*ACT1))/B1M
      PCO2=ZH2CO3/BMEN
      CSP=ZCA*ZCO3*(ACT2*ACT2)
      C1M=(ZH*ZHCO3*(ACT1*ACT1))/(ZH2CO3)
      C2M=(ZH*ZCO3*ACT1)/(ZHCO3)
      TCA=ZCA+ZCASO
      STCO2=ZH2CO3+ZHCO3+ZCO3
      AIABK=ALOG10(ZNA*ACT1)+2.*ALOG10(ZSIO2)+PH-(.348+.88323*TEMP)
      AMK=ALOG10(ZK*ACT1)+2.*ALOG10(ZSIO2)+PH-(.31629+TEMP*2.931)
      AAMK=ALOG10((ZCA*ACT1)+PH-(10.84-.37114*TEMP)
      AIK=.5*ALOG10(ZK*ACT1)+.25*ALOG10(ZMG*ACT2)+1.2*ALOG10(ZSIO2)
     1    +1.1*PH-(1.892-.005856*TEMP)
      ACAMK=.1666+(ALOG10((ZCA*ACT2)+8.*ALOG10(ZSIO2)+2.*PH-(.01143*
     1    TEMP-16.6))
      AKC=2.*ALOG10(ZSIO2)-(.02*TEMP-6.79)
C     CONVERT MOLALITY TO PPM .
      ZCA=ZCA*40.08E3
      ZMG=ZMG*24.32E3
      ZNA=ZNA*22.991E3
      ZK=ZK*39.102E3
      ZH2CO3=ZH2CO3*62.E3
      ZCO3=ZCO3*60.E3
      ZCACO=ZCACO*100.09E3
      ZSO4=ZSO4*96.06E3
      ZHCO3=ZHCO3*61.E3
      ZMGSO=ZMGSO*110.38E3
      ZNASO=ZNASO*120.056E3
      ZCASO=ZCASO*136.14E3
      ZCL=ZCL*35.457E3
      WRITE(6,14) ZCA,ZMG,ZNA,ZK
      WRITE(6,15) ZH2CO3,ZHCO3,ZCO3,ZSO4,ZC.
      WRITE(6,16) ZCACO,ZMGSO,ZNASO, ZCASO
      WRITE(6,17) EQPH, ACT1, ACT2, SIC, SID
      WRITE(6,202) PCO2,SIG
202   FORMAT(/,1X,$PCO2=$,E10.2,2X,$SATG=$,E10.2)
14    FORMAT(/,1X,$CALCULATED CATION CONCENTRATIONS(PPM)$,
     1/,1X,$CA=$,F10.2,2X,$MG=$,F10.2,2X,$NA=$,F10.2,2X,$K=$,F10.2)
15    FORMAT(/,1X,$CALCULATED CARBONATE AND ANION CONCENTRATIONS
     1(PPM)$,/,1X,$H2CO3=$,F10.2,2X,$=CO3=$,F10.2,2X,$CO3=$,
     2F10.2,2X,$SO4=$,F10.2,/,1X,$CL=$,F12.2)
16    FORMAT(/,1X,$CALCULATED ION PAIR CONCENTRATIONS(PPM)$,
     1/,1X,$CACO3=$,F10.2,2X,$MGSO4=$,F10.2,2X,$NASO4=$,F10.2,
     12X,$CASO4=$,F10.2)
17    FORMAT(/,1X,$EQUIL PH=$,F5.2,3X,$ACT1=$,F5.2,3X,$ACT2=
     1$,F5.2,3X,$SIC=$,E10.2,2X,$SID=$,E10.2)
      WRITE(6,23) AIABK,AMK,AAMK,AIK,ACAMK,AKC
28    FORMAT(/,1X,$I(AB-K)=$,E10.2,1X,$I(AF-K)=$,E10.2,1X,$I(AN-K)=
     1 $,E10.2,/,1X,$I(IL-K)=$,E10.2,1X,$I(CM-K)=$,E10.2,1X,$I(K-
     1G)=$,E10.2)
      WRITE(2,19)
18    FORMAT(/,1X,$ANY MORE DATA?$)
      READ(1,19) ANS
19    FORMAT(A3)
      IF(ANS.EQ.3HYES) GO TO 100
999   STOP
      END
```